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MINIMUM PRINCIPLE FOR A NONEQUILIBRIUM STOCHASTIC SYSTEM

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Synopsis

An urn model of a linear stochastic system is investigated. By imposing a boundary condition, the regular addition or removal of balls from certain urns, a steady nonequilibrium distribution can be induced. The quantity which is a minimum when the state of the system is steady is the square of the difference of the contents of two urns, multiplied by the probability of transfer between the urns and summed over all urn pairs. The minimum quantity is approximately equal to the entropy production rate if the departure from equilibrium is small.

1. Introduction. The equilibrium state of a thermodynamic system is the state for which the entropy is a maximum. This principle contains the information that the mechanism of transition from one state to another plays no part in determining the equilibrium distribution. Although an extremum [illegible] of a statistical system could not [illegible] ication, the subject is [illegible]

[illegible] does not take the most [illegible] develop [illegible] have described a living organism as such a system and have suggested that the complexity of organisms may be better understood if it is realized that such systems do not take the most probable state.(1)

In the development of macroscopic irreversible thermodynamics, it has been found that the steady state of some systems can be described by the principle that the rate of entropy production is a maximum.(2) Malkus has applied this principle to a turbulent flow problem with some success.(3)

The minimization of an integral was used to obtain approximate solutions for the Chapman-Enskog approximation to the Boltzmann equation(4) even before Prigogine identified this integral as the kinetic theory representation (to the same approximation) of the entropy production rate.(5)

An urn model of a linear stochastic system is described below. Boundary conditions are imposed which require a steady transport through the system. The quantity which is a maximum for the steady configuration of the model can be described as the product of the microscopic fluxes and forces in the model. This quantity is a source term for a balance equation. It can be identified with the entropy production rate only when the system is close to equilibrium.

2. The Urn Model. Imagine a system consisting of several urns and a large number of balls. The balls are numbered consecutively and distributed among the urns, each of which is designated by a letter. A number is chosen at random and the corresponding ball is removed from the urn in which it is found and placed in another urn. If a ball is drawn from the ith urn, then the probability that the urn in which the ball is subsequently placed is the jth urn is denoted p_{ij}. The probabilities p are required to satisfy microscopic reversibility, $p_{ij} = p_{ji}$. The ensemble average of the rate

of change of the number of balls in an urn is given by equation (1).

$$\frac{dn_i}{dt} = \sum_j \frac{n_j}{N} p_{ji} - \frac{n_i}{N} \sum_j p_{ij}$$
$$= \sum_j \frac{n_j - n_i}{N} p_{ij} \qquad (1)$$

where n_i is the number of balls in the ith urn,

$\frac{dn_i}{dt}$ is the average change in n_i per drawing,

and N is the total number of balls in all urns.

This system was introduced by the Ehrenfests to clarify the meaning of Boltzmann's H theorem.[6]

$$H = \sum_i n_i \ln n_i \qquad (2)$$

$$\frac{dH}{dt} = \sum_i \frac{dn_i}{dt} \ln n_i$$

$$= -\sum_{i,j} p_{ij} (n_j - n_i) \ln \frac{n_j}{n_i} \leq 0 \qquad (3)$$

The system exhibits an irreversible behavior as expressed by Boltzmann's H theorem. The unsteady behavior of the system as it approaches equilibrium from arbitrary initial conditions has been studied by several authors[7][8][9].

3. The Nonequilibrium State. A steady nonequilibrium configuration can be produced by applying certain boundary conditions. For instance, a ball may be periodically added or removed from a given urn. Then,

$$\frac{dn_i}{dt} = \sum_j \frac{n_j - n_i}{N} p_{ij} + \alpha_i \tag{4}$$

where α_i is the average number of balls added to the ith urn per drawing and $\sum \alpha_i = 0$.

Consider the quantity β .

$$\beta = \sum_{i,j} \frac{n_i(n_j - n_i)}{N} p_{ij} \tag{5}$$

$$= -\frac{1}{2} \sum_{i,j} \frac{(n_i - n_j)^2}{N} p_{ij} \leq 0 \tag{6}$$

For a small change in the state of the system,

$$\delta\left(\beta + 2\sum_i \alpha_i n_i\right) = 2\sum_i \left\{\sum_j \frac{(n_j - n_i)}{N} p_{ij} + \alpha_i\right\}\delta n_i + O\left(\frac{\delta n_i \delta n_j}{N}\right) \tag{7}$$

Requiring $\left(\beta + 2\sum \alpha_i n_i\right)$ to be stationary with respect to any small change of the state of the system δn_i is equivalent to finding the steady solution to equation (4).

The flux of particles from the ith to the jth urn is $(n_i - n_j) p_{ij}/N$. The quantity $(n_i - n_j)$ is a measure of the force driving this flux. Therefore, β may be considered as the sum of the products of the microscopic fluxes and forces in the system.

Multiplying equation (4) by n_i and summing over all i results in equation (8)

$$\frac{1}{2} \sum_i \frac{dn_i^2}{dt} = -\frac{1}{2} \sum_{ij} \frac{(n_i - n_j)^2}{N} p_{ij} + \sum_i \alpha_i n_i \tag{8}$$

Here β appears as a source term for the quantity $B = \frac{1}{2} \sum n_i^2$. The flux of B through the boundaries of the system is given by $\sum \alpha_i n_i$. B must decrease monotonically in an isolated system.

The quantities B and β may be identified with the entropy and entropy production rate if the system is very close to equilibrium. For $n_i = n_0(1+\epsilon_i)$ and $\sum \epsilon_i = 0$,

$$S = -\sum_i n_i \ln n_i \approx -\sum_i \left(n_0 \ln n_0 + \frac{1}{2} n_0 \epsilon_i^2\right) \tag{9}$$

$$(S - S_0) \approx -(B - B_0)/n_0 \tag{10}$$

Similarly,

$$\sigma = -\sum_i \frac{dn_i}{dt} \ln n_i \approx -\beta/n_0 \tag{11}$$

The identification holds to order ϵ_i^2.

A minimum principle which characterizes the steady state of a linear stochastic system has been found, but for a system which is far from equilibrium, the entropy production rate is not a minimum.

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References

1. Prigogine, I. and Wiame, J. M., Experientia, 2, 451 (1946).
2. de Groot, S. R. and Mazur, P., Nonequilibrium Thermodynamics, North Holland Publishing Company, Amsterdam (1962).
3. Malkus, W. V. R., Jour. Fluid Mech., 1, 521 (1956).
4. Hellund, E. J. and Uehling, E. A., Phys. Rev., 56, 818 (1939).
5. Prigogine, I., Physica, 15, 272 (1949).
6. Ehrenfest, P. and Ehrenfest, T., Phys. Zeit., 8, 311 (1907).
7. Schrödinger, E. and Kohlrausch, F., Phys. Zeit., 27, 306 (1926).
8. Kac, M., Amer. Math. Monthly, 54, 369 (1947). Reprinted in Wax, N., Selected Papers on Noise and Stochastic Processes, Dover Publications, Inc., New York (1954).
9. Klein, M., Physica, 22, 569 (1956).